



# Photocatalytic reduction of Pb(II) over TiO<sub>2</sub>: New insights on the effect of different electron donors

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## ABSTRACT

Experiments of Pb(II) photocatalytic removal under nitrogen over TiO<sub>2</sub> (Degussa P-25) were performed in the presence of electron donors such as methanol, ethanol, 2-propanol, citric acid (Cit) and formic acid (FA) in order to study their effects on the removal efficiencies. Formic acid and 2-propanol showed the highest effect, but the first one was considered a better additive because it can be used at a concentration five-fold lower and it does not introduce toxic degradation products in the system. In the case of formic acid addition at low concentration, redissolution of Pb was observed when the electron donor was completely consumed. Product formation was dependent on the reaction conditions and on the nature of electron donor, but the main identified product in all cases was zerovalent Pb, in the form of colloidal particles, as demonstrated by XRD and XPS analysis. Mechanisms involving reducing radicals were proposed to explain Pb(II) removal and the comparative efficiency of the donors.

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## 1. Introduction

Lead has been related to several toxicological effects on human health and behavioral alterations; even death cases by lead poisoning were reported [1]. An epidemiological study demonstrated that there is a close correlation between the average lead concentration in tap water and blood lead concentration [2]. WHO established in 10 µg L<sup>-1</sup> the maximum allowable value for Pb in drinking water [3], while the Maximum Contaminant Level Goal has been set at zero by the US EPA, indicating the extreme potential toxicity of lead [4].

Methods for lead removal from water are precipitation as carbonate or hydroxide, chelation with complexing organic acids and further precipitation, electrolysis, chemical oxidation [5], and even by adsorption on coffee grounds [6]. Ionizing radiation (γ-radiolysis, e-beam irradiation) has also been proposed to be used to remove lead from aqueous solutions, and enlightening experiments in the presence of scavengers of hydroxyl radicals (HO•) allowed elucidating the nature of the species formed in these processes and aspects on the formation of colloidal lead ([7–12] and references therein). However, most of the above treatments

are expensive, and other ways of lead elimination from wastewater have to be investigated and developed.

Heterogeneous photocatalysis (HP) with TiO<sub>2</sub> and UV light is an emergent technology able to destroy or transform a variety of pollutants by oxidative or reductive mechanisms. The process provides a rapid procedure for removal of toxic organics and even microbiological pollution. In recent years, the high potentiality for photocatalytic transformation of metal ions, including recovery of valuable metals, has started to be studied [13]. In this sense, HP can be envisaged as a convenient method for eliminating Pb(II) from aqueous solutions, although the process and its mechanistic features have not received enough attention [14–20]. The mechanisms of transformation of lead(II) in water by UV-TiO<sub>2</sub> are especially attractive because they depend very much on the reaction conditions, related to the nature of the photocatalyst, presence or absence of oxygen and presence of electron donors. In a recent paper, we initiated investigations trying to analyze the features of this system, studying the effect of oxygen, nitrogen, ozone, platinization of TiO<sub>2</sub> and 2-propanol addition [21]. Reference [20] reports experiments of UV and visible photocatalytic reduction of lead over titania based binary oxide materials in several conditions including the presence of some organic compounds. However, the photocatalytic materials are different from those used in the present paper and no mechanistic evidences are presented.

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In the present work, the effect of different organic electron donors on Pb(II) photoreduction and lead deposition at TiO<sub>2</sub> particles is presented, proposing possible mechanisms. This study points out to explain differences on Pb(II) conversion in terms of a profound analysis of the mechanisms taking place in different experimental conditions, which was not done in previous papers. The effect of the nature of each donor is analyzed, aiming to take advantage of these differences in real systems, where dissolved lead and organic pollutants coexist.

## 2. Experimental

### 2.1. Chemicals

TiO<sub>2</sub> (Degussa P-25) was provided by Degussa AG Germany and used as received. Lead(II) was added as Pb(NO<sub>3</sub>)<sub>2</sub> (Merck). 2-Propanol (2-PrOH) was Merck; methanol (MeOH) and ethanol (EtOH) were both Mallinckrodt. Formic acid (FA) and citric acid (Cit) were Analyticals (99%) and Riedel de Haën, respectively. HClO<sub>4</sub> was used for pH adjustments. All reagents were of the highest purity and used without further purification.

Deionized water (Barnstead E-pure, resistivity = 18 MΩ cm) was used for preparation of solutions and suspensions.

### 2.2. Photocatalytic experiments

Irradiations were performed as published elsewhere [21]. Briefly, TiO<sub>2</sub> suspensions (1 g L<sup>-1</sup>, 450 mL) containing 0.5 mM Pb(II) and the corresponding electron donor at preset concentrations were recirculated (1.5 L min<sup>-1</sup>) from a reservoir through an annular reactor, inside which a black light tubular lamp (Philips FL15 BLB, 15 W, 300 < λ/nm < 450) was installed. Suspensions were bubbled with N<sub>2</sub> (2 L min<sup>-1</sup>) throughout the experiments, and adjusted and maintained at pH 3 by HClO<sub>4</sub> addition, except indicated. Actinometric measurements were performed by the ferrioxalate method. A photon flux density ( $q_p/V$ ) of 7.3 μeinstein s<sup>-1</sup> L<sup>-1</sup> was calculated. In one experiment, a different irradiation setup, with a lamp external to the reactor, was used. This setup consisted of a thermostatted cylindrical glass cell (V = 30 mL) provided with a Teflon cap with a gas inlet, a sampler and a holder for a 300–400 nm bandpass filter (Schott Catalog #BG25, thickness 3 mm, maximum transmission (80%) at 390 nm). 10 mL of a TiO<sub>2</sub> suspension (1 g L<sup>-1</sup>), containing 0.5 mM Pb(II) and 0.2 M HCOOH, were introduced in the cell, and irradiation was applied from the top using a high-pressure xenon arc lamp (Osram XBO, 450 W). A 60-mm pathlength water filter was used to remove the IR fraction of the light. N<sub>2</sub> was bubbled during the run. A photon flux density ( $q_p/V$ ) of 20.9 μeinstein s<sup>-1</sup> L<sup>-1</sup> was calculated for this setup.

In all runs, the suspensions were stirred for 30 min in the dark before irradiation to reach the adsorption equilibrium of Pb(II) and donors onto TiO<sub>2</sub>. A decrease in Pb(II) concentration in the range 2–7% was observed in the different runs. This value was discounted to take into account only changes due to light irradiation. No additional adsorption of lead(II) on the catalyst was observed in any case after prolonged stirring in the dark. No changes in Pb(II) concentration in solution were measured under irradiation in the absence of photocatalyst.

All photocatalytic and dark experiments were performed at 25 °C.

### 2.3. Analytical determinations

Pb(II) concentration changes were measured by colorimetry with 4-(2-pyridylazo)-resorcinol (PAR reagent) at 520 nm [22]. As citric acid interferes in this method, probably because it complexes

Pb(II) at pH 2 [23], lead was evaluated in this case by inductively coupled plasma optical emission spectrometry (ICP-OES) [24]. The other additives do not interfere with PAR.

The mineralization degree of the organic compounds was followed by total organic carbon analysis, using a Shimadzu 5000 A TOC analyzer in the non-purgeable organic carbon (NPOC) mode.

### 2.4. Analysis of solid residues

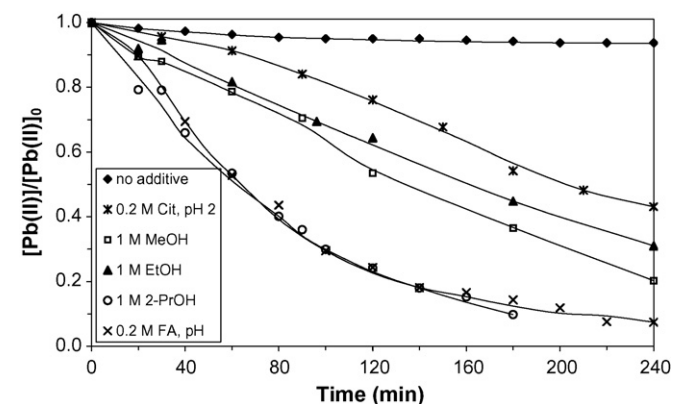
Deposits found at the end of the runs were analyzed by SEM-EDS (Philips 515), XRD (Philips PW-3710 diffractometer) and XPS (VG ESCA3 Mark II), previous drying under N<sub>2</sub> atmosphere.

XPS measurements were carried out using the MgKα line (1253.6 eV) as incident radiation. The binding energies were calibrated considering the Au 4f<sub>7/2</sub> peak at 83.9 eV with respect to the Fermi level. The shift of the binding energy due to surface charging effect was calibrated by assuming the binding energy of C 1s to be always 284.6 eV. Assignations of species were supported by quantitative analysis performed using XPS Multiquant Version 4.10.39 Program. The sample was analyzed before and after bombardment with Ar<sup>+</sup> (1 min, 5 μA current target, 5 kV energy) in order to remove any impurities. XPS lines of Pb 4f, O 1s, C 1s and Ti 2p were recorded. Spectral deconvolution was accomplished for each narrow spectrum by using XPSPEAK Version 4.1 software for XPS curve fitting.

## 3. Results

### 3.1. Photocatalytic experiments

Fig. 1 shows the results of photocatalytic experiments of Pb(II) (0.5 mM) at the indicated initial pH (pH<sub>0</sub>) using pure TiO<sub>2</sub> under N<sub>2</sub>. The fraction of Pb(II) in solution, [Pb(II)]/[Pb(II)]<sub>0</sub>, is plotted against the irradiation time [Pb(II)]<sub>0</sub> being the initial concentration after discounting the amount adsorbed in the dark. Photocatalytic runs in the presence of alcohols (1 M) were performed at pH 3 (constant throughout the run); experiments with 0.2 M formic and citric acid were done at the original pH of the suspensions, namely, ~2.3 and ~2, respectively, also maintained constant during the experiment. Oxalic acid was also tested as a possible enhancing electron donor, based on the work of Tennakone and Wijayantha [25]. To avoid precipitation of lead oxalate [26], the experiment was performed at a very low oxalic acid concentration (0.010 mM, pH 3), but no lead removal was observed in these conditions (data not shown).

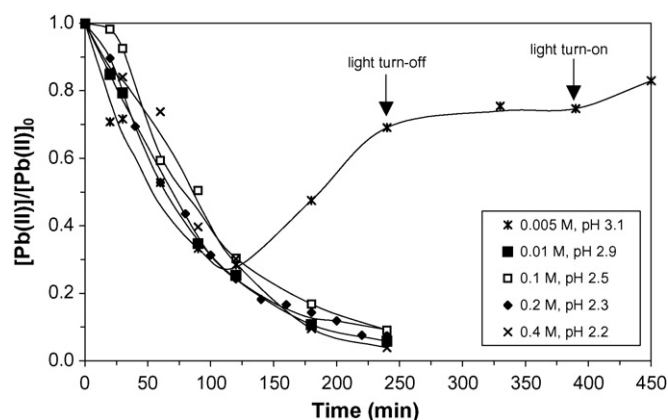


**Fig. 1.** Time profiles of normalized Pb(II) concentration in the presence of different electron donors during TiO<sub>2</sub> photocatalytic runs under N<sub>2</sub>. Curve in the absence of additives is also shown. Conditions: [Pb(II)]<sub>0</sub> = 0.5 mM, [TiO<sub>2</sub>] = 1 g L<sup>-1</sup>, N<sub>2</sub> = 2 L min<sup>-1</sup>, pH<sub>0</sub> 3 (except indicated),  $q_p/V$  = 7.3 μeinstein s<sup>-1</sup> L<sup>-1</sup>.

Our results are in agreement with previous works [17–19]. In the absence of additives, almost negligible Pb(II) removal (6% at 240 min) took place. Among the alcohols, 2-propanol exerts the highest effect, followed by MeOH and EtOH, and FA is much more efficient than Cit. Although FA and 2-PrOH led to similar removal extent, the effect of FA is more important taking into account that it is used at a five-fold lower concentration. An additional advantage is that it will not produce toxic intermediates (like aldehydes or ketones) because it degrades directly to CO<sub>2</sub>. In some cases, an induction period is clearly seen, the largest being the case of Cit. This effect can be due to rests of oxygen remaining in the system, which inhibit Pb(II) reduction, as seen previously in radiolytic experiments [7,10]. All the curves, except the one in the absence of additives, exhibited a rather good pseudo-first order kinetics (after the induction periods in the corresponding cases), with correlation factors higher than 0.95. In contrast with our results, Kabra et al. [27,28] reported 41.7% of Pb(II) removal with citric acid at pH 2, but they concluded that the deposition was merely adsorptive. In our case, Pb(II) removal was indeed photoinduced (57% after 240 min), because, as mentioned before, no additional removal in the dark was observed after 30 min. Although Kabra et al. used different experimental conditions (a lower [Pb(II)], a higher TiO<sub>2</sub> mass), the main reasons for the discrepancy with the present work is surely that they did not exclude oxygen from the system and that pH was not kept constant during the experiments.

As FA was the most efficient donor, the effect of changing progressively its concentration in the 0.4–0.005 M range was investigated. The initial pH of the runs was the original one, and it was kept constant during the experiment by HClO<sub>4</sub> addition. Fig. 2 shows that donor concentration hardly influences Pb removal; good exponential time profiles, confirming the pseudo-first order, were observed (after induction periods in some curves). In contrast to the other concentrations, at 0.005 M FA, a regrowth of Pb(II) concentration in solution after 120 min of irradiation was observed. In this experiment, irradiation and N<sub>2</sub>-bubbling were stopped at 240 min; subsequent sampling indicated almost no changes in Pb(II) concentration in the following 150 min. The lamp and N<sub>2</sub>-bubbling were restarted at 390 min, and a new increase of [Pb(II)] took place. These results suggest a light-induced reoxidation promoted by exhaustion of donor in the suspension, as judged by NPOC results (see later), and by the fact that pH had to be controlled more frequently than in the other cases, indicating a rapid FA consumption and CO<sub>2</sub> formation (see Table 1).

Rate constants, taken from the plots (calculated after the induction periods), are shown in Table 1. They reflect the abovementioned activity. Results indicate that for FA, rate



**Fig. 2.** Time profiles of normalized Pb(II) concentration in the presence of different FA concentrations during TiO<sub>2</sub> photocatalytic runs under N<sub>2</sub>. Conditions: [Pb(II)]<sub>0</sub> = 0.5 mM, [TiO<sub>2</sub>] = 1 g L<sup>-1</sup>, N<sub>2</sub> = 2 L min<sup>-1</sup>;  $q_p/V = 7.3 \mu\text{einstein s}^{-1} \text{L}^{-1}$ .

**Table 1**

Pseudo-first order rate constants of Pb(II) removal and percentage of NPOC decrease

Electron donor	$k$ (min <sup>-1</sup> )	NPOC decrease at 120 min (%)	NPOC decrease at 240 min (%)
None	0.0008 <sup>a</sup>	–	–
MeOH	0.0087	0	0
EtOH	0.0057	0	11
2-PrOH	0.0134	11	16
0.4 M FA	0.0169	1	1
0.2 M FA	0.010	0	0.1
0.1 M FA	0.0098	8	11
0.01 M FA	0.0125	49	67
0.005 M FA	0.0116	ND	96
0.2 M Cit	0.0047	0	2

Data of Figs. 1 and 2. [Alcohol]<sub>0</sub> = 1 M.

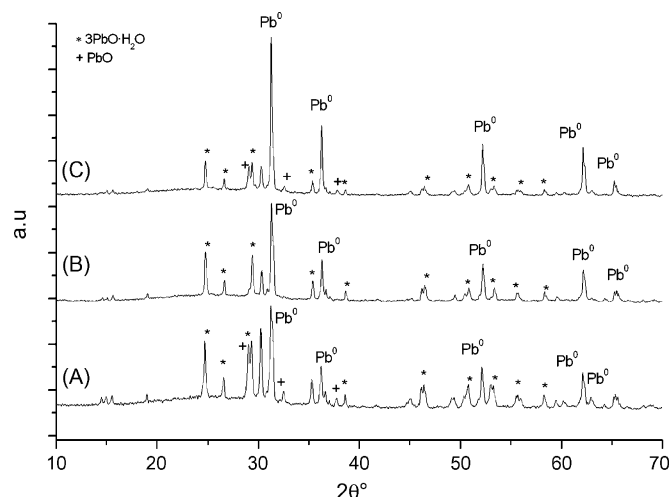
<sup>a</sup> Initial rate constant (only the first three points of the curve were taken and fitted to an exponential).

constants were rather similar for all concentrations, the differences being in the limits of error (and perhaps slightly influenced by different pH<sub>0</sub>). Negligible mineralization was observed in all cases, with the exception of the systems with 2-propanol (low extent) and formic acid at low concentrations. Particularly, at 0.005 M, after 240 min of irradiation, NPOC decreased under the detection limit of the method ( $\sim 1 \text{ mg C L}^{-1}$ ).

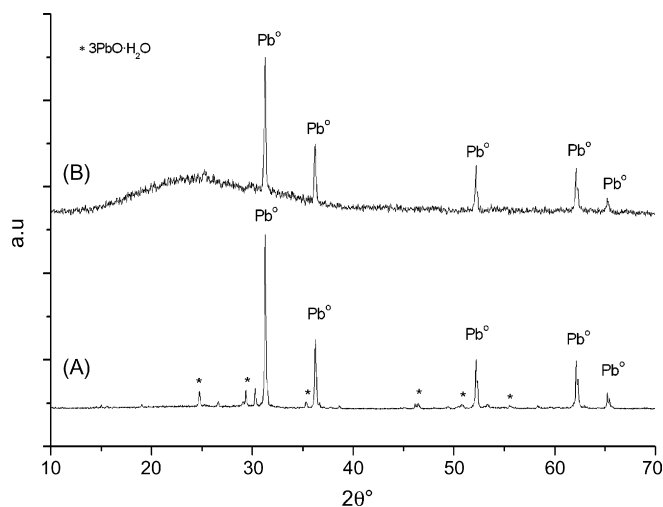
### 3.2. XRD analysis

After the photocatalytic experiments, dark gray spots were observed on the lamp surface in the presence of all donors. In order to identify the photoproducts, XRD analysis was performed on this material and on the filtered catalyst particles. In the last case, XRD patterns corresponded always to pure P-25, without signals of Pb compounds (not shown).

As can be seen in Fig. 3, patterns of deposits on the lamp obtained in the runs with ethanol and 2-propanol showed peaks of Pb(0), PbO and a hydrated lead oxide, 3PbO·H<sub>2</sub>O, while in the case of the experiments with methanol only Pb(0) and 3PbO·H<sub>2</sub>O appeared. In the experiments with MeOH and EtOH, many dark fine particles were found in the suspension, in addition to the deposits on the lamp, which can be attributed to metal clusters. Barkatt and Rabani [29], Ershov et al. [8], and Belloni et al. [30], among others, effectively observed colloidal Pb formation in radiolytic experiments in the presence of organic compounds.



**Fig. 3.** XRD patterns of solid residues deposited on the lamp surface after photocatalytic runs under N<sub>2</sub> in the presence of donors: (A) 2-PrOH, (B) MeOH and (C) EtOH. Spectra were intentionally shifted for appropriate comparison.



**Fig. 4.** XRD patterns of solid residues deposited on the lamp surface during the photocatalytic runs under  $N_2$ : (A) 0.1 M FA ( $pH_0 \sim 2.5$ ) and (B) 0.2 M Cit ( $pH_0 \sim 2.0$ ). Spectra were intentionally shifted for appropriate comparison.

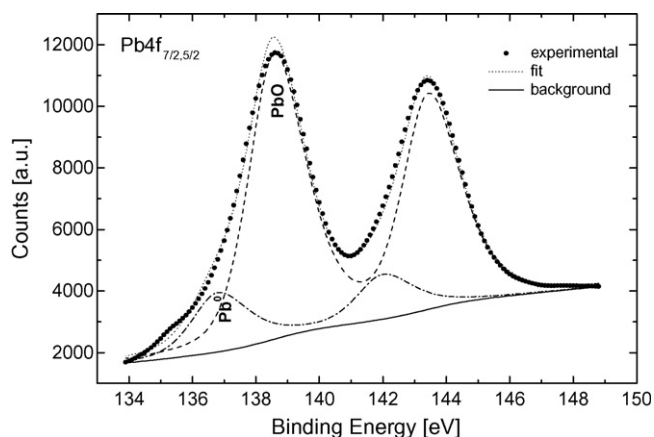
Fig. 4 shows XRD patterns of deposits obtained in runs with FA and Cit. In the first case (A), Pb(O) formation is conclusive but other peaks can be assigned to  $3PbO \cdot H_2O$ . In the second case (B), only peaks corresponding to Pb(O) were present. No peaks corresponding to lead formate, lead oxalate or  $Pb(CO_3)_2$  were observed in any of the XRD diagrams.

### 3.3. SEM-EDS analysis

Fig. 5 shows micrographs of suspended particles or deposits found in experiments with MeOH and EtOH. Photographs coming from runs with methanol (Fig. 5A) show suspended filiform particles composed only of lead. In contrast, with ethanol, the lead-containing particles seem to be amorphous (Fig. 5B). In both cases, Pb-containing particles formed a phase separated from  $TiO_2$ , i.e., particles did not contain simultaneously Ti and Pb.

### 3.4. XPS analysis

Deposits obtained in runs carried out in presence of ethanol were analyzed by XPS in order to identify the chemical lead species in the reaction products. An initial analysis (spectrum not shown) revealed signals corresponding to Pb  $4f_{7/2}$  and  $4f_{5/2}$  photoelectrons at



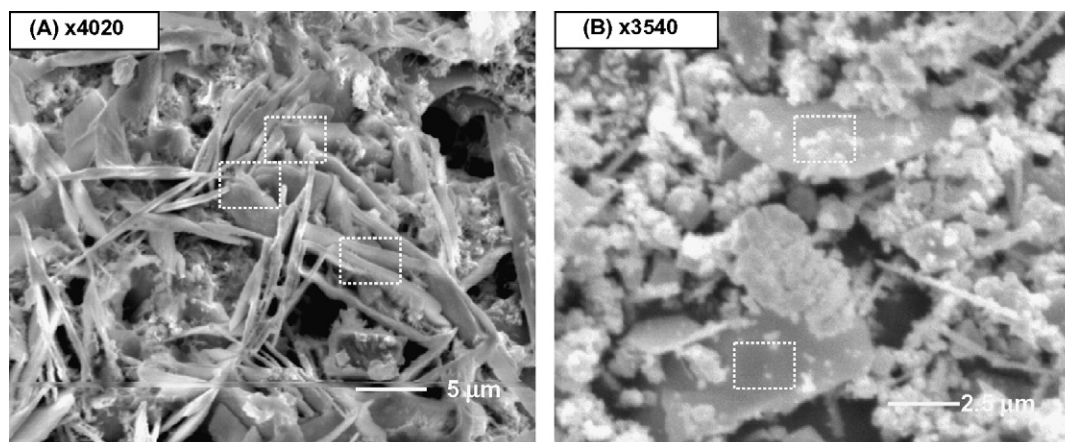
**Fig. 6.** X-ray photoelectron spectra of Pb  $4f_{7/2,5/2}$  levels for photodeposits after a run in the presence of ethanol. Material was exposed to  $Ar^+$  bombardment.

138.6 eV and 143.4 eV, respectively, in good agreement with reported values [31]. Since the Pb  $4f_{7/2}$  binding energies are specific to various Pb oxidation states [31], deconvolution of this peak was attempted. Only one compound could be fitted and, according to the energy found, 138.6 eV, the signal was assigned to PbO, in agreement with the value of 138.9 eV reported in Ref. [32]. A second analysis was made after  $Ar^+$  bombardment (in order to remove any contaminants from the sample surface). By deconvolution, a new peak at 136.8 eV was observed (Fig. 6), which could be related to Pb(O), according to the values of 136.3 eV and 136.8 eV reported by Chenthamarakshan et al. [17] and Kanai et al. [33], respectively. According to this information, it can be concluded that Pb is partially and quickly oxidized when manipulating the sample, in spite of precautions taken during the examination; this coincides with findings of other authors [34,35].

Fig. 7 shows experimental and deconvoluted spectra of the O 1s XPS line, after  $Ar^+$  bombardment. The contribution of three peaks can be seen. The one at 529.4 eV is attributed to  $TiO_2$ , while those at 530.6 eV and 532.0 eV can be attributed to PbO and adsorbed oxygen, which might correspond to different oxygen species (e.g., other lead oxides or hydroxides), respectively.

## 4. Discussion

According to the proposed mechanism of HP, irradiation of  $TiO_2$  suspensions by photons of energy higher than that of the



**Fig. 5.** Electronic photographs of deposits and suspended particles after photocatalytic runs under  $N_2$  in the presence of electron donors. (A) MeOH and (B) EtOH. Dotted squares indicate places where EDS analysis was performed.



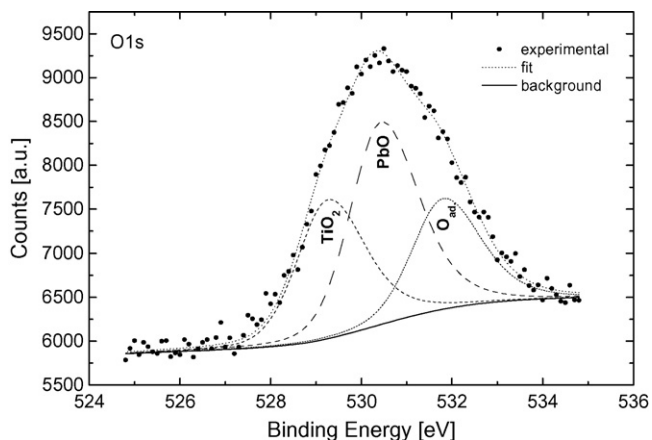


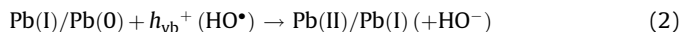
Fig. 7. X-ray photoelectron spectra of O 1s level for deposits on the lamp after a run in the presence of ethanol obtained after Ar<sup>+</sup> bombardment.

semiconductor band gap leads to promotion of electrons into the TiO<sub>2</sub> conduction band ( $e_{cb}^-$ ), leaving simultaneously positive holes in the valence band ( $h_{vb}^+$ ):

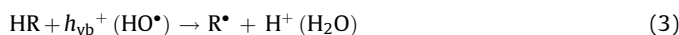


According to Ref. [36], conduction band electrons and valence band holes of Degussa P-25 at pH 3 have redox positions at  $-0.5 \text{ V}^1$  and  $+2.7 \text{ V}$ , respectively. Hydroxyl radicals ( $\text{HO}^\bullet$ ) ( $E(\text{HO}^\bullet/\text{H}_2\text{O}) = +2.6 \text{ V}$ ) can be formed by hole attack on water or surface hydroxyls and, in turn,  $\text{HO}^\bullet$  radicals or holes can oxidize other species present in the system.

In our previous work [21], we made an extensive discussion about possible mechanisms involved in the photocatalytic reaction of Pb(II) over TiO<sub>2</sub> under different conditions. As photocatalytic processes proceed usually by mono-electronic steps, it can be proposed the formation of the unusual Pb(I) oxidation state, identified in radiolytic reductive processes [7,8,37,38], by reduction of Pb(II) by conduction band electrons of the excited semiconductor. However, in the case of TiO<sub>2</sub>, this pathway is negligible in the absence of electron donors, even under nitrogen, due to two main reasons: (1) the reduction potential of Pb(II) to Pb(I) is much more negative than that of  $\text{TiO}_2 - e_{cb}^-$  ( $-1.0 \text{ V}$  [7]), and although the second mono-electronic reductive step ( $E(\text{Pb(I)}/\text{Pb(0)}) = +0.75 \text{ V}$ ) [7] does have a enough positive potential to be driven by  $e_{cb}^-$ , it is the first mono-electronic step that limits the success of the global reduction of Pb(II) to Pb(0); 2)  $\text{HO}^\bullet$  or holes have enough positive reduction potentials to reoxidize Pb(I) and Pb(0) shortly after being produced:



Addition of alcohols or other organic compounds (HR) accelerates the reduction due to the formation of highly reductive radical species ( $\text{R}^\bullet$ ) generated by  $h_{vb}^+$  or  $\text{HO}^\bullet$ :



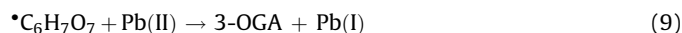
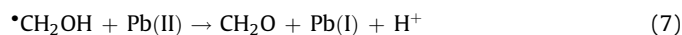
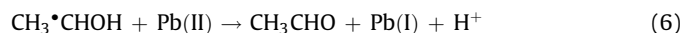
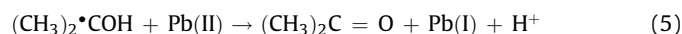
Concurrently, reaction (2) will be hindered in these conditions because reaction (3) predominates; rate constants of reaction of  $\text{HO}^\bullet$  with all donors used in this paper are at least one order of magnitude higher than that with Pb(II) [39]; in addition, reaction (3) will be favored because HR have been added at relatively high concentrations. For the reduction potentials of HR/ $\text{R}^\bullet$  couples, the

following values of the early work of Lilie et al., based on polarographic determinations, were taken [40]:  $0.97 \text{ V}$  for methanol,  $1.15 \text{ V}$  for ethanol,  $1.3 \text{ V}$  for 2-propanol (all at pH 3), and  $1.3 \text{ V}$  for formate (at pH 2.3). The value for citric acid at pH 2 would be approximately  $1.7 \text{ V}$  [41]. According to this, the oxidation of all these compounds by  $\text{HO}^\bullet$  or holes to the corresponding  $\text{R}^\bullet$  will be thermodynamically favorable. The conjugated cathodic reaction is  $\text{H}^+$  reduction by  $e_{cb}^-$ , with  $\text{H}_2$  formation. It is important to note that  $\text{H}_2$  production over pure irradiated TiO<sub>2</sub> is not a thermodynamically favorable process [42], judged by the electrode potential for mono-electronic reduction of  $\text{H}^+$  to  $\text{H}^\bullet$  ( $-2.3 \text{ V}$  at pH 0 [7]); the process may be slightly enhanced in the presence of alcohols or other electron donors and in reductive conditions, but the origin of the activity is still not very clear [43,44].

Once produced,  $\text{R}^\bullet$  would be the effective reducing species of Pb(II):



where  $\text{R}_{\text{ox}}$  is an aldehyde, ketone or  $\text{CO}_2$  depending on the initial compound (reactions (5)–(9)). Even formation of complexes between  $\text{R}^\bullet$  and Pb(I) has been proposed [7].



where  $^\bullet\text{C}_6\text{H}_7\text{O}_7$  represents the free radical formed from Cit, and 3-OGA is 3-oxoglutaric acid, one of products of Cit oxidation [45,46]. For the reduction potentials of  $\text{R}_{\text{ox}}/\text{R}^\bullet$  couples, the values given by Breitenkamp et al. have been taken [7], i.e.:  $-1.6 \text{ V}$ ,  $-0.9 \text{ V}$  and  $-0.8 \text{ V}$  for the derivatives of 2-propanol, ethanol, methanol (all at pH 3), and  $-1.8 \text{ V}$  for  $\text{CO}_2^{\bullet-}$  at pH 2.3, respectively [7]. The values for the radical species evolved from citric acid (several possibilities [45,46]) are not known, but, analogously to the other donors, they are probably more negative than  $-1 \text{ V}$ .

The final step of the process is the easy reduction of Pb(I) to Pb(0) (the stable product) by the reducing radicals or by conduction band electrons.

Methanol and ethanol are interesting because the corresponding reduction potentials are slightly more positive than that of the Pb(II)/Pb(I) couple (i.e., the thermodynamic driving force for the electron transfer is about 0). In spite of this, when methanol or ethanol in high concentrations were added to the suspension, reduction of Pb(II) to Pb(0) was observed; this will be explained later. Taking into account the abovementioned approximate one-electron reduction potential of the donors at the pH<sub>0</sub> of each run, although a strict correlation cannot be done, it is apparent that the rate constants of Pb(II) removal (Table 1) depend on these potentials. Moreover, the fact that a very high concentration of alcohols is necessary to produce changes, as seen in our previous paper [21], but only low amounts of FA and Cit are enough, can be due to the different nature of the electron donors: carboxylic acids, able to adsorb or even form complexes with the TiO<sub>2</sub> surface may act as hole scavengers, while alcohols may act mainly as  $\text{HO}^\bullet$  scavengers, as proposed earlier by Prairie et al. [47].

The synergetic effect of the donors is clearly seen in the experiment with  $0.005 \text{ M}$  FA (Fig. 2), where Pb(II) removal from the suspension takes place while the donor is present, but, after its consumption, lead begins to be reoxidized by holes or  $\text{HO}^\bullet$  (reaction (2)). When the light is off, Pb redissolution stops, and it

<sup>1</sup> All reduction potentials ( $E$ ) cited in this work are vs. NHE at  $1 \text{ M}$  concentrations and at pH 3, except indicated. Electrode potentials in aqueous solution are cited; on the TiO<sub>2</sub> surface they can be somewhat different.

reinitiates under restarting irradiation, suggesting the occurrence of a light-induced reoxidation process promoted by exhaustion of donor in the suspension; this is demonstrated by TOC results.

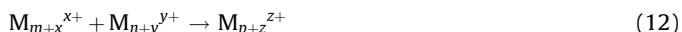
In our experiments, Pb(0) was found as a product of the photocatalytic processes, as proved by XRD, SEM-EDS and XPS. Zerovalent lead was accompanied in all cases, except for the Cit system, by lead oxides, formed probably by reoxidation during the manipulation of the samples before analyses. As shown in Fig. 5, the photoproducted Pb(0) appeared as a separate phase from that of TiO<sub>2</sub>. Similar behavior of formation of separate particles was observed in other cases [48,49]. As in the presence of citric acid only Pb(0) was detected, this indicates that this electron donor would produce a stabilizing effect on nascent lead atoms, avoiding subsequent partial reoxidation when exposing the deposited material to the atmosphere. This phenomenon does not take place with the other additives, but it is reported that some ligands (e.g., CN<sup>-</sup>, EDTA) are able to stabilize small-sized particles [30].

It is worth mentioning that when formic acid was the electron donor, catalyst particles become lightly sky-blue under irradiation, turning visibly colorless during filtration in air. This color was not observed in runs carried out in the dark. Similar behavior has been observed with when Ag<sup>+</sup> solutions were radiolytically irradiated in the presence of 2-propanol and polyacrylate as stabilizer [30]. Henglein et al. [9] observed a maximum at 660 nm in the spectrum obtained after pulse radiolysis of solutions of Pb(ClO<sub>4</sub>)<sub>2</sub>, which they attributed to the formation of lead atoms (naked or complexed by Pb<sup>2+</sup>, i.e., Pb<sub>2</sub><sup>2+</sup>). The color could be attributed also to Ti(III) (e<sub>TiO<sub>2</sub></sub><sup>-</sup>) formed during photocatalytic processes in the absence of oxygen [42,50].

As described in the literature [8,30,48,51], the process of Pb(II) (or other metal ions) reduction is complex, and unusual phenomena take place when nascent metal particles are formed, including creation of clusters, and their sticking together building colloidal particles. It was suggested that atoms dimerize when they encounter or associate with an excess of ions:



By a multi-step process, these species progressively coalesce into clusters:



where *m*, *n* and *p* represent the nuclearities (number or reduced atoms) and *x*, *y* and *z* are the number of associated ions [30].

It is informed that the size of Pb clusters formed by radiolysis ranges 2–15 nm [30]. We propose a similar size in our case. From these clusters, colloidal particles are generated, which, in the absence of stabilizing admixtures (e.g., surfactants), are unstable, and after few seconds they coagulate and precipitate, forming larger metallic particles. While the clusters are long-lived in the absence of air, they are very sensitive to traces of oxygen before agglomeration and dissolve readily in air; however, after agglomeration, they become practically unreactive to O<sub>2</sub> [7,30].

What is really important is that the nascent particles (Pb<sub>2</sub>, etc.) are reported to have thermodynamic properties distinct from those of the bulk metal, e.g., reduction potentials less negative than those of the radicals [30,51]. The reported value of −1.0 V corresponds to *n* = 1 in the following reaction:



but this value was calculated to shift rather gradually toward more positive potentials with increasing nuclearity (*n*) [51,52]; the calculated value for *n* = 4 is around 0 V. This explains why reducing

radicals cause so important synergetic effect and are successful for the transformation of Pb(II) to Pb(I), including those derived from methanol and ethanol, whose reduction potentials are just somewhat more positive than −1 V. This evidence could even explain why there is some reaction when no electron donor is added, as observed by us and others [17]. Disproportionation processes cannot be either discarded.

Formation of lead particles separated from those of TiO<sub>2</sub> would also indicate that reaction between R<sup>\*</sup> and Pb(II) takes place in solution and not at the surface. To confirm this hypothesis, an additional test was made with 0.2 M FA, using a setup with an external lamp. In this case, no lead removal occurred, but the suspension turned blue during the run indicating reaction; interruption of nitrogen bubbling made the suspension to return to the white color.

## 5. Conclusions

A careful study of the reduction of Pb(II) by TiO<sub>2</sub> photocatalysis under UV irradiation under nitrogen in the presence of several electron donors confirms that the reaction is very dependent on the nature and concentration of the donors and that the main product of the photocatalysis is zerovalent lead. The species begins to be formed in clusters like the case of other metals (e.g., Ag), then agglomerating until the formation of metallic particles. Although the reaction is inhibited by oxygen, this method, especially in the case of the addition of formic acid, could be useful to treat lead contamination in aqueous water effluents, which generally contain organic matter that can be degraded to formate (or other donors) under photocatalytic reactions.

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